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NO_x - SOURCES, PROPERTIES AND ANALYTICAL PROCEDURES

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<p>→ This report is to provide the propellant combustion product characterization community with a general background on the chemistry, sources, properties, and health effects of nitrogen oxides (NO_x) and to present the analytical procedures and types of instrumentation currently available for measuring NO_x. The NO_x atmospheric cycle with emphasis on conversion reactions of nitric oxide (NO) to nitrogen dioxide (NO₂), the anthropogenic and naturally occurring sources, and the properties of NO_x in the context of propellant emissions of NO_x are discussed. The toxicity of NO and NO₂ is described. The common methods of measuring NO_x are explained in generic terms. There are two appendices: one is a table which aids in determining the most suitable method of measuring NO_x, and the other is a list of addresses of manufacturers of NO_x analyzers.</p>					
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INTRODUCTION

Over the past two decades there has been a sharp increase in awareness of the presence of oxides of nitrogen (NO_x) in the Earth's atmosphere. Nitrous oxide (N_2O) is the most abundant of the NO_x . The other oxides of nitrogen are Nitric Oxide (NO), nitrogen dioxide (NO_2), nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5). Nitrogen dioxide and NO , both free radicals, are the most toxic of the NO_x , with NO_2 being by far the most toxic. Anthropogenic sources of NO_x in urban areas have produced levels of NO and NO_2 high enough to cause health problems. Because NO_x are among the propellant combustion products of military weapons systems, the U.S. Army is concerned about the exposure of its personnel to these compounds.

The sampling and analysis of NO_x from military sources offers unique challenges as regards to both sampling and instrumentation. Calibration and analysis are usually performed under field conditions, which present obstacles such as vibration, temperature and humidity fluctuations, and airborne dust. Other important considerations are portability, ease and rapidity of set-up and calibration, and the overall size of an instrument.

Operating military weapons systems is very expensive and available space for instruments used in monitoring is limited. Because of the expense, research involving the monitoring of combustion products from military weapons systems must be scheduled during training exercises. The scheduling is seldom at the discretion of the analyst, and measurements must be performed within the confines of the training schedule. This often results in time constraints that minimize the opportunity to gather potentially significant data. An example of a space constraint is that resulting from the need to place instrumentation inside the narrow crew compartments of armored vehicles.

Aside from the foregoing obstacles, the very nature of gun smoke presents considerable analytical challenges. Owing to the variety and amount of combustion products, interferences with the analytical procedure must be carefully considered.

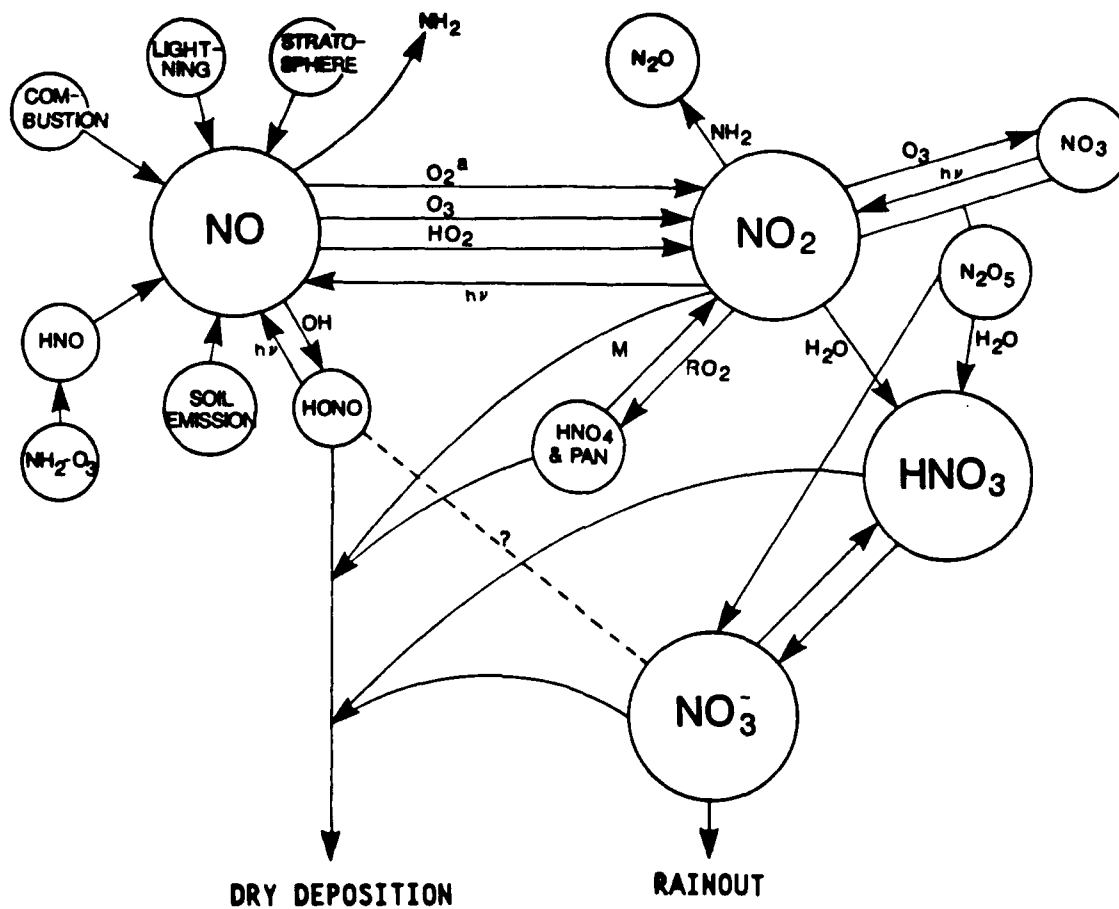
The ultimate goal of monitoring toxic gases under field conditions is to estimate human exposure levels. These estimates are needed if one is to accurately predict health hazards and performance decrements associated with the firing of various weapons systems. Because the operators of these weapons systems are close to the sources of the combustion products, they can be exposed to short bursts of relatively high levels of toxic gases that have not yet been diluted by mixing with the surrounding atmosphere. Therefore, the best results are obtained by sampling the toxic gases near operator breathing zones on a real-time basis.

The purpose of this report is to provide the propellant combustion product characterization community with a general background on the sources, chemistry, and health effects of NO_x and to present the analytical procedures and types of instrumentation currently available for measuring NO_x .

CHEMISTRY AND KINETICS

Nitrogen oxides are involved in a very complex cycle of atmospheric reactions that are simplified below in Figure 1:¹

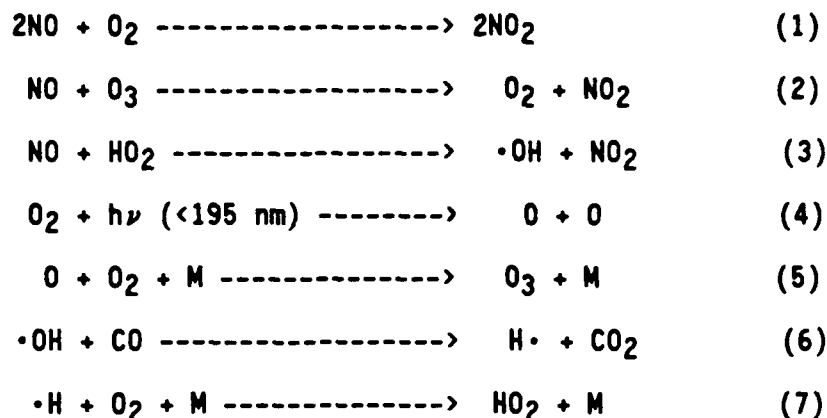
Figure 1. Simplified Diagram of the NO_x Atmospheric Cycle



^a, added by authors

(Stedman and Shetter, 1983)

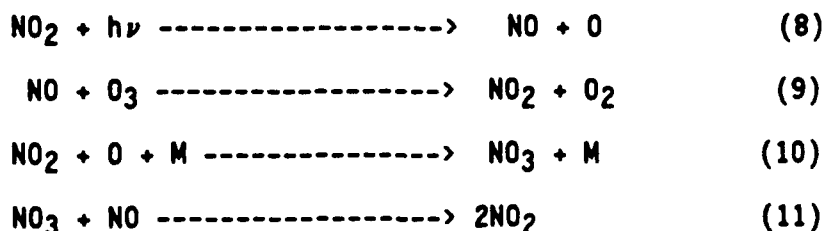
The diagram shows that NO results from direct sources whereas NO is produced by conversion reactions. The conversion reactions of NO to NO₂ occur in daylight and are shown below along with the major side reactions:²



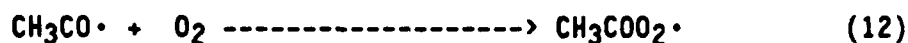
Reaction 1 is very slow at NO concentrations below 0.5 parts per million (ppm) but is very fast (in the order of 15 percent/minute) at the high concentrations of NO (500 ppm) found immediately following processes such as conventional gas combustion.² Reactions 4 and 5 provide the O₃ to drive reaction 2. In terms of reactivity, the ·OH radical is the major atmospheric oxidant and is found at a globally averaged concentration of (7.7 ± 1.4) × 10⁵ radicals per cm³.³

Rapid conversion of NO to NO₂ occurs in a CO polluted atmosphere through reactions 6 and 7, which drive reaction 3. This sequence of reactions, along with other mechanisms, limits the NO half-life in the troposphere from the order of seconds to as long as a few minutes.⁴ Therefore, the amount of NO₂ formed, and thus the ratio of NO₂ to NO, depends greatly on the concentration of the NO and the presence of CO during irradiation.

Reaction 2 is involved also in the NO_x catalytic cycle, which is the major chemical destruction mechanism of stratospheric ozone.⁵ Ozone in the stratosphere acts as a protective layer by filtering out some of the ultraviolet radiation from the sun. In the natural balancing process the NO catalytic chain may destroy over half of the ozone. However, the NO_x introduced into the atmosphere from anthropogenic sources have caused a shift in the natural balancing process of ozone, leading to its depletion.⁶ The following are the major reactions in the NO_x catalytic chain, with reaction 8 driving the process and reaction 11 regenerating the NO₂ broken down in reaction 8:²

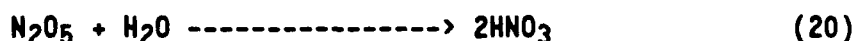
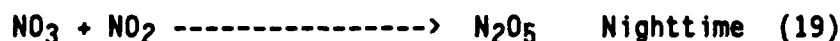
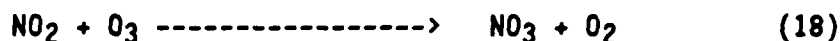
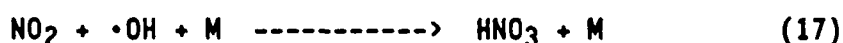
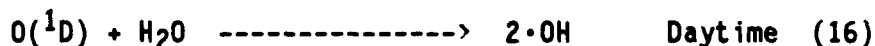
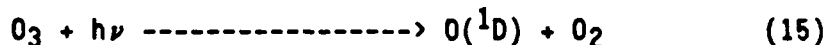


A major pollutant in smog, peroxyacetyl nitrate (PAN) is produced after a long sequence of reactions involving the acetyl radical from acetaldehyde, oxygen, and NO₂:²



Reaction 14 is the summation of reactions 12 and 13.² PAN is a powerful lachrymator and the main eye-irritant found in smog. It is also one of the most abundant oxidation products of smog because acetaldehyde is an oxidation product of virtually all n-alkanes and n-alkenes.²

Nitrogen dioxide reacts rapidly with the hydroxyl radical ($\cdot\text{OH}$) during the daytime to produce nitric acid (HNO_3), which is the cause of acid rain in some areas. Nitric acid is produced also at night, but O_3 is involved rather than $\cdot\text{OH}$. The daytime and nighttime sequence of reactions leading to HNO_3 production have as rate-limiting steps reactions 17 ($2.6 \times 10^{-30} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$) and 19 ($2.2 \times 10^{-30} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$):^{6,7}



NO and NO₂ are recycled easily and, therefore, are discussed in terms of atmospheric chemistry as NO_x. Nitrogen oxides have been estimated to have a lifetime of less than one day in the summer and a few days in the winter.⁶ Thus, it is thought that PAN, which is very stable in the colder regions of the middle and upper troposphere, may act as a reservoir and carrier for NO_x. PAN releases NO_x under warmer conditions, inasmuch as the temperature-dependent equilibrium between NO_x and PAN favors higher concentrations of NO_x. Thus, as the mass of air warms in a strong seasonal cycle or a change in regional climates, the upper tropospheric reservoir of PAN could transport NO_x to lower altitudes and lower latitudes.⁸

SOURCES AND PROPERTIES OF NO_x

Whether naturally occurring or anthropogenic, the most common forms of NO_x are NO, NO₂, and the relatively nonreactive N₂O. Some physical properties of the major NO_x constituents are listed below.

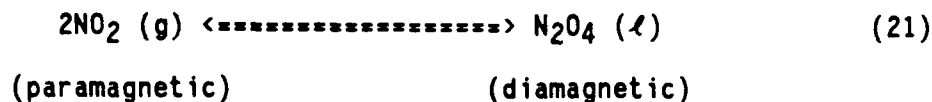
Table 1. Physical Characteristics of NO_x

Species	Molecular Weight g/mole	Solubility in Water cm ³ /100g ^{a,b}	Melting Point °C	Boiling Point °C ^{a,b}
NO	30.01	7.34	-163.6	-151.7
NO ₂	46.01	reacts w/H ₂ O forming HONO ₂ and HONO	liquid and solid forms are primarily N ₂ O ₄	
N ₂ O ₄ (dimer of NO ₂)	92.02	130.52	-11.3	21.2
N ₂ O	44.02	130.0	-102.4	-89.0

^a Matheson Gas Data Book (at STP)

^b Handbook of Chemistry and Physics

In the gas phase, NO₂ (deep red-brown) and N₂O₄ exist in a strongly temperature-dependent equilibrium:



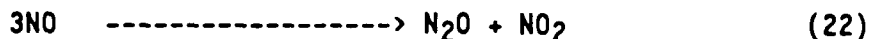
The ΔH°_{298} for dissociation is 57 kJ mol⁻¹. As a solid, the oxide is completely N₂O₄. At the melting point N₂O₄ dissociates to the extent of 0.01 percent NO₂. There is further dissociation to 0.1 percent NO₂ in the deep red-brown liquid at the boiling point. In the vapor state at 100°C, N₂O₄ is 90 percent dissociated, and virtually completely dissociated at 140°C. Nitrogen dioxide has an unpaired electron associated mainly with the N atom, which is lost fairly readily (IP = 9.91 eV) to give the nitronium ion (NO₂⁺). There are three isomeric forms of the dimer of NO₂. The planar form is by far the most stable (O₂N--NO₂). The other known form is found at -196°C and it is the twisted nonplanar form of O₂N--NO₂, and there are indications that the third form is planar ONONO₂ found at --259°C.⁹

Total emissions of NO_x from natural and anthropogenic sources are between 34 and 74 x 10¹² gm of N/year. Between 5 and 11 percent of the total NO_x formed is produced by lightning. Microbial activity accounts for 11 to 16 percent. Combination reactions involving molecular oxygen and nitrogen in the presence of UV-irradiation in the stratosphere account for about 2 percent.⁷

Anthropogenic sources are all the more significant when they are localized in urban areas or dwellings. Kitchen appliances such as gas stoves or heaters, and cigarette smoke can account for unhealthy levels of NO_x in a home.¹⁰ In urban areas fossil fuel combustion from motor vehicles and the burning of coal, oil, and natural gas make up about 40 percent of NO_x emission. These sources can elevate urban concentrations by as much as 100 times the levels found in nonurban areas. Biomass burning, mostly from clearing forests for farm and other uses, produces another 30 percent.⁷

The production of NO in conventional combustion chambers is strongly dependent on temperature. Combustion at temperatures below 1200 K produces negligible amounts of NO; at 2200 K, NO production reaches a maximum.¹¹ Fossil fuel combustion forms NO by the oxidation of nitrogen in the fuel and in the atmosphere. In the higher temperature regions of the combustion chamber, NO is formed from atmospheric nitrogen, while fuel nitrogen is oxidized in the regions of lower temperature. Depending on combustion chamber design, fuel atmospheric nitrogen can be a major source of NO emissions.¹²

The NO_x emission from the combustion of fossil fuels is in the form of NO. It is then converted to NO_2 within minutes by O_3 and by O_2 as shown by reactions 1 and 2 and by the decomposition of NO to N_2O and NO_2 as shown by reaction 23, which occurs at temperatures in the range of 30 to 50° C and at pressures above one atmosphere.^{2,9}



The formation of NO occurs at a slower rate than the combustion process and therefore the production of NO continues into post-combustion. The formation rate, besides being dependent on the combustion temperature, is dependent also on oxygen concentration. The rapid cooling of combustion gases prevents the return of NO to N_2 and O_2 , even though thermodynamic equilibrium favors the latter increasingly as temperature decreases.

The NO is converted also to NO_2 through photochemical reactions involving hydrocarbons, miscellaneous hetero compounds, and intermediate free radicals generated by uv-irradiation in polluted atmospheres, and most importantly by ozone (O_3). These reactions also produce a variety of secondary pollutants and in totality are responsible for photochemical smog. Thus, atmospheric reactions leading to photochemical smog are initiated by emission of NO_x . The major characteristic of this smog is its oxidative nature.¹²

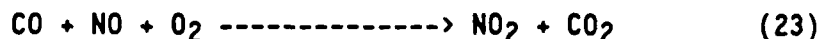
The concentrations of constituents found in exhaust emissions from military weapons depend on the propellant formulations, igniters, primers, temperatures of combustion, pressures in the weapon barrels and erosion of metals in gun barrels and combustion chambers.¹³ In studies of propellant burn products, NO_x have been found in various concentrations. There were too many variables from study to study to permit the formulation of accurate combustion models. The NO_x found in gun exhaust primarily comes from the decomposition of nitrates and nitrocompounds used in propellants.¹³ In a recent investigation, 75 g of M-36 propellant was burned and NO concentrations were found at an average level of 3.5 ppm.¹⁴ In other research, analysis of an XM-

19 propellant burn showed NO_x to be below detectable limits when a thermal conductivity detector (TCD) was used with gas chromatography.¹⁵

Investigators at The Bureau of Mines monitored emissions at various distances from a flat grid-type flame and found large amounts of CO_2 coupled with significant amounts of NO_2 . Also, they found that the measured values were much higher than the predicted values. It was hypothesized that after burning or secondary explosions after the exhaust gases had mixed with air in the test stand apparatus resulted in further NO_x formation; this explanation has not been confirmed. The study also showed that the extreme cooling rates found in guns prevented an increase in NO_x formation above the initial value in the primary combustion zone. With rapid cooling, it also appears that the degree of oxidation of CO to CO_2 is substantially less than that predicted thermodynamically.¹⁶

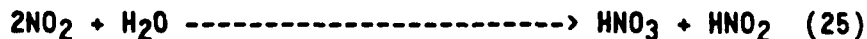
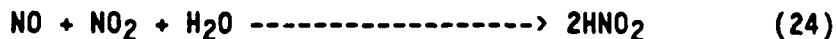
A study by Goshgarian (1976) using a micrometer combustion chamber led to an accidental but interesting finding.¹⁷ Instead of the usual absence of NO_x , NO appeared following a rapid reduction in chamber pressure when a blow-out valve ruptured. It was speculated that the drop-in pressure caused rapid cooling,¹⁷ which prevented dissociation of NO to elemental nitrogen and oxygen.

Smog chamber experiments have shown that CO affects the rate of oxidation of NO in an $\text{NO-NO}_2\text{-H}_2\text{O}$ -air system during uv-irradiation. In the presence of CO, NO is rapidly converted to NO_2 . This occurs through a chain mechanism driven by the reactive OH radical in reaction 6.² Reaction 23 is the summation of reactions 6, 7, and 3.



HEALTH EFFECTS OF NO_x

The harmful effects of NO_x are largely attributed to NO_2 , the most toxic of these oxides. Nitrogen dioxide, which has a Threshold Limit Value (TLV) of 5 parts per million (ppm), exerts its primary toxic effects on the lungs via free radical-mediated reactions and other mechanisms.¹⁸ Both NO, which has a TLV of 25 ppm, and NO_2 , as free radicals, may initiate lipid peroxidation reactions in the cell.^{18,19} Nitric oxide not converted to NO_2 in air may react with NO_2 and water to form HNO_2 as shown in Reaction 24.⁹ Nitrogen dioxide similarly reacts with H_2O , as shown in Reaction 25, but forms HNO_2 and nitric acid (HNO_3), which is more acidic than HNO_2 .⁹



The greatest danger of NO_2 exposure is in the delay of its full effect upon the respiratory system. Before one experiences such symptoms as weakness, coldness, headache, nausea, dizziness, abdominal pain, cyanosis, or severe convulsions and unconsciousness, one may already have received a lethal dose.¹⁸ Death is caused by pulmonary edema or bronchiolitis fibrosa obliterans.¹²

The delayed effect of NO_2 injury is made even more dangerous by two other factors. First, human perception of the odor of NO_2 is not sufficient to warn against injury or even death in some circumstances. Sensitive individuals can smell 0.12 ppm of NO_2 , but an average person only responds to concentrations above 0.22 ppm. Furthermore, NO_2 quickly desensitizes an individual to its odor, and if NO_2 levels gradually rise, a person could unknowingly be exposed to concentrations high enough to cause permanent injury or death. In fact, with a gradually increasing concentration of NO_2 (as might occur in a confined space), olfactory perception may not occur until concentrations have reached 25 ppm. On sudden exposure to higher concentrations up to 4.0 ppm, the olfactory response is expunged within 1 to 10 minutes and returns within 1 to 1.5 minutes only if the person is removed from the NO_2 -contaminated environment.^{10,12} Therefore, the sensory warning properties for NO_2 are inadequate. The irritative effects of NO_2 also occur gradually and are not immediately perceived.^{10,20,21} The second factor has to do with the low water-solubility of NO_2 . Since it is not highly water-soluble, it is only slowly removed from the lungs by circulating blood and may remain in contact with lung cells for prolonged periods of time.¹⁸

Given the same total dose, short-term exposure to high concentrations of NO_2 is more injurious than long-term exposure to lower concentrations.¹⁰ The toxic effects of NO_2 are often synergistic with or additive to those of other toxic contaminants. The presence of other oxidants, harmful pollutants, or infectious bacteria serves to lower the concentration of NO_2 necessary to produce a specific toxic effect.^{10,18}

Some groups of people are more sensitive to the effects of NO_2 than the general population. One way of determining the injurious effects of NO_2 on the health of subjects is to measure airway resistance during respiration by a forced oscillatory technique before and after exposure to NO_2 . Exposure to NO_2 has been shown to increase airway resistance and possibly reduce oxygen exchange in the lungs in healthy individuals.¹⁰ Other studies cited in this review have indicated that asthmatics, children, persons with pre-existing respiratory disease, and healthy exercising subjects are more sensitive to oxidant exposure than healthy inactive individuals.¹⁰ Interestingly, healthy persons are more sensitive to oxidant-polluted air during exercise than are resting persons with chronic respiratory diseases such as asthma.^{22,23}

INSTRUMENTATION

CHEMILUMINESCENT 24

The most common chemiluminescent technique for monitoring NO_x involves the reaction between NO and O_3 . This involves reducing NO_2 to NO , then measuring total NO_x as NO . Interferences occur because other nitrogen species, such as HNO_3 and PAN, are reduced to NO . Another technique involves the photodissociation of NO_2 to form NO and then the chemiluminescent reaction with O_3 ; here, the aforementioned interferences do not occur.

Recently, NO_2 detectors have been developed that depend on the chemiluminescent reaction between NO_2 and luminol (5-amino-2,3-dihydro-1,4-phthalazinedione). With this type of detector, NO can be monitored following

oxidation to NO_2 . PAN and O_3 interfere slightly with such an NO_2 measurement, although interference by O_3 is minimized by directing the air sample through pyrex wool coated with 5 percent polyunsaturated hydrocarbons. Interference by PAN is still a problem, but is presently being addressed. Sample air is drawn continuously into an inlet with a valve to direct sample airflow. The sample airflow can be directed into an NO_2 scrubber (FeSO_4 trap), providing "zero" air to the reaction chamber with the same characteristics (except for absence of NO_2) as the sample. Another option is to direct airflow into a trap where NO is oxidized to NO_2 and then directed to the reaction chamber so as to measure total NO_x . A third option is to pass the "zero" air through a permeation tube calibration device in which changes in flow rate determine the concentration of NO_2 delivered to the reaction chamber. The final option is to deliver the sample airflow directly to the reaction chamber so as to measure just NO_2 . The luminol reagent is continuously pumped into a cell or over a wick and the light emitted by the reaction is measured by a photometer. The electronic signal output is amplified and sent to a recorder or to a data acquisition system. Maximizing the luminol surface area increases sensitivity and results in good response even at a low air sample flow rate.

COLORIMETRIC

Jacobs-Hochheiser Method for NO_2 ²⁵

This method is used for sampling ambient air containing NO_2 . In this detection method, ambient air is drawn through an aqueous sodium hydroxide solution for periods as long as a day. Nitrogen dioxide gas is converted by the sodium hydroxide to sodium nitrite. Hydrogen peroxide (H_2O_2) is added to remove any SO_2 interferences prior to acidification. The resulting HNO_2 is reacted with sulfanilamide to form a diazonium salt, which is then coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) to form a deep red azo dye. The color is measured at 540 nm and compared to standards prepared in similar fashion.

Christie (Arsenite) Method for NO_2 ²⁶

This method is quite like the Jacobs-Hochheiser method, the only difference being that NO_2 is trapped in a sodium hydroxide-sodium arsenite solution to produce a stable solution of sodium nitrite. The nitrite ion is then reacted with the same reagents used in the Jacobs-Hochheiser method to produce a measurable color change. The standard sampling period is 24 hours, and samples remain stable for 6 weeks. Collection efficiency is about 85 percent, and small amounts of positive NO interference have been reported.

Levaggi Method for NO_2 ²⁷

The Levaggi triethanolamine (TEA) method also is similar to the Jacobs-Hochheiser procedure. The difference between the two procedures is that, in the Levaggi TEA method, NO_2 is absorbed in a TEA solution or a TEA-impregnated molecular sieve for a 24-hour sampling period. The efficiency of absorption is reported to be 95 percent with both liquid and solid absorbers. Interference by SO_2 is not observed in experiments with the liquid absorber, while slight interferences from SO_2 occur when a solid absorber is used.

Phenoldisulfonic Acid (PDS) Method for NO₂ ²⁸

In the PDS method an air sample is drawn into a collection flask of known volume which has been evacuated to the vapor pressure of the strongly oxidizing absorption solution (H₂O₂ in 0.1N sulfuric acid). The species NO, NO₂, N₂O₃, N₂O₄, and HNO₃ are oxidized by the absorption solution to the nitrate ion (NO₃⁻). The solution is then made alkaline with sodium hydroxide and evaporated to dryness. The resulting solids are dissolved in an acid solution to form nitrophenoldisulfonic acid, which is measured at 410 nm. The intensity of absorption is proportional to the amount of nitrate. This method is best suited for measuring from a few parts per million to a few parts per trillion of total NO_x; however, the PDS method is time consuming and is not continuous.

Saltzman Method for NO₂ ²⁹

The Saltzman diazotization procedure is the most often used colorimetric method in the determination of NO₂ gas concentration. The gas is trapped in an impinger containing an aqueous or an alkaline aqueous solution of TEA. The NO₂ gas is thereby converted to nitrite. A solution of acidic sulfanilamide is added to the nitrite, whereby a diazonium salt is formed. N-(-1-Naphthyl)-ethylenediamine dihydrochloride (NEDA) is then added; it complexes with the diazonium salt to form a purple azo dye that is normally stable for weeks. The dye's color intensity is proportional to the concentration of nitrite and thus to the absorbed NO₂.

A method of calibrating the procedure involves determining the absorption efficiency of the species in the trapping solution. A calibration curve is produced with nitrite standards. Values derived from the calibration curve are multiplied by an efficiency factor. The factor, called the Saltzman factor, was determined by Saltzman to be 0.72. However, other studies indicate a factor between 0.6 and 1.2, depending on such atmospheric conditions as humidity, temperature, and particulate matter inspired into the trapping solution. A quicker method of calibration, using NO₂ permeation tubes, permits removal of the efficiency step. Since this calibration step is a direct comparison to an NO₂ gas concentration, it represents an improvement in accuracy and precision.

Flow Injection Analysis (FIA) Method for NO₂ ³⁰

A more recent development in the colorimetric determination of NO₂ gas is the use of FIA and miniature impinger technology. A continuous-stream miniature impinger is used to trap NO₂ gas in an aqueous phase containing a combined Saltzman diazotization reagent consisting of 26 mL of concentrated hydrochloric acid, 0.5 g NEDA, and 5.0 g of sulfanilamide in 1.0 L of H₂O. When NO₂ gas is present, an immediate color change occurs, which is monitored continuously with a colorimeter set at 540 nm. The response time is less than 6 seconds, whereas previous colorimetric analyzers response times were on the order of a few minutes. The improved response time is due to the use of a smaller impinger (reduced dead volume) and to FIA technology that permits reproducible measurement of color before maximum color intensity has been

reached. The procedure shows good linearity from 1 to 10 ppm for NO_2 with an r^2 (square of the linear regression coefficient) value of 0.9996.

ION CHROMATOGRAPHIC (IC) 31

The use of IC for measuring NO_2 is quick, simple, and sensitive with low background effects. To measure NO_2 , air is drawn through a Sep-Pak^R C18 cartridge impregnated with TEA. The trapped NO_2 is removed by passing a buffer solution through the cartridge. The NO_2 is detected as a total of nitrite (NO_2^-) and nitrate (NO_3^-) ions determined by IC.

ION SELECTIVE ELECTRODE 32

The ion-selective electrode method for measuring NO_x in the form of NO_3^- produces quick and accurate results. The potential of the electrode corresponds to the concentration (activity) of ions as indicated by the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln a$$

E^0 , constant standard potential of the cell

R, gas constant

T, absolute temperature

F, is the Faraday constant

n, is the ionic charge

a, is the ionic activity of the cell (related to concentration)

The liquid ion-exchange membrane electrode is the most common NO_3^- ion-selective electrode. The logarithm of the NO_3^- activity (essentially the concentration) is proportional to the response in millivolts. Ion-selective electrode measurements are rapid, in the range of 1 to 2 minutes. There is some positive interference from sulfate ion at $\text{SO}_4^{2-}/\text{NO}_3^-$ mole ratios above 50. The ion-selective electrode method has the advantages of speed and simplicity.

ELECTROCHEMICAL 33

Electrochemical sensors are available for the detection of NO_2 . The NO_2 is adsorbed onto a gold electrode where electrooxidation occurs. The current required to oxidize the NO_2 is proportional to the concentration of NO_2 . This method of testing produces good selectivity, high accuracy, high reproducibility, short response time, and continuous monitoring for NO_2 .

GAS CHROMATOGRAPHIC 34

The gas chromatographic method for NO_x depends on the operation of a separation column. Adsorption columns are packed with a porous solid material, and partition columns are packed with a solid impregnated with a liquid. A column has a carrier gas stream continuously flowing through it usually comprised of helium. The sample to be analyzed is injected into the carrier gas just before the column. Components of the sample gas are

separated by the column packing material. The separated components pass through a detector and produce a signal recorded as a function of time. The amount of a specific component present is proportional to the area under the response peak. As regards NO and NO₂ detection, complex gas chromatographs have been developed. Their major drawbacks have been poor sensitivity and low reliability in ambient air monitoring.

SPECTROSCOPIC

Infrared (IR) Method for NO_x 35, 36

In modern IR spectrophotometers all wavelengths of IR radiation are emitted by a laser light source. The radiation is split by mirrors into two beams, the reference beam and the sample beam. The two beams are passed through the sample and enter into the chopper, which is another mirror system. The chopper produces a single continuous beam from the reference and sample beams by alternating from reference beam to sample beam. The alternating beam is diffracted by a grating that separates the beam into its different wavelengths. The detector measures the difference in intensities of the two segments of the beam at each wavelength. The difference in intensities of the sample and reference beams at the wavelength each particular NO_x species absorbs is quantified by comparison to known concentrations of the NO_x species.

The main problem with IR spectroscopy is that the strength of the energy sources available for irradiation is limited. Other problems are the costs of equipment and specialized training for operators of the instrumentation. Many new techniques and instruments are being developed in the IR spectroscopy field.

Ultraviolet (UV) Method for NO₂ 37

Ultraviolet absorption and emission spectra are useful for identifying NO₂ and other pollutants that undergo photo-chemical reactions by comparison to spectra of standards. Each photochemically reactive gas exhibits its own unique set of absorption wavelengths. Nitric oxide, which does not absorb UV light, is measured in terms of the NO₂ to which it is first converted. The UV wavelength of maximum absorption (λ_{\max}) of NO₂ is 448 nm.

New Advances in Spectroscopy

Two new methods of spectroscopy that are commonly used to measure NO₂ gas are the tunable diode laser (TDL) method and the differential absorption lidar (DIAL) method. The TDL uses the IR region of the spectrum and DIAL uses the UV region of the spectrum. Each method has been undergoing rapid development; here, their descriptions will be kept general.

TUNABLE DIODE LASER (TDL) 38, 39

The TDL radiation source is scanned over a narrow wavelength region around the absorption line of interest. Tuning the output is usually done by changing the temperature. Also, it can be done by varying the magnetic field or the hydrostatic pressure of the gas sample.

Since the spectral irradiance of a diode laser is 10^8 to 10^{12} times more intense than a thermal source, most measurements are not limited by detector noise, allowing a longer path length to be used. In the amplitude modulated (AM) mode, the laser beam is chopped mechanically, and the transmitted power is detected at the chopping frequency. In the frequency modulated (FM) mode, the laser output frequency is rapidly modulated about the wavelength of interest. The FM mode eliminates much of the background noise and is capable of measuring absorbencies as low as .001 percent absorbance units compared to 1 percent for the amplitude modulated mode.

DIFFERENTIAL ABSORPTION LASER (DIAL) 40

The DIAL method is used more than the TDL method because it compensates for scattering of the laser beam and the attenuation by other absorbing species. A pair of lasers are used to produce a pair of beams of different wavelength which are directed through the sample and reflected from a distant target. The differential absorption of the two wavelengths is computed and used to determine the gas concentration.

The UV region of the spectrum is most often used in the DIAL method because of the large absorption bands of CO_2 , H_2O , and other atmospheric trace gases in the IR region of the spectrum. The DIAL method allows for the detection of NO_2 as low as 100 parts per trillion when a 10 km path length is used. Several species of gases can be measured simultaneously.

Both techniques, TDL and DIAL require expensive equipment, time-consuming expert operations, and long analysis times. However, both methods are very specific for NO_2 and other species.

CONCLUSION

This study was conducted in order to provide the propellant combustion product characterization community with a general background on the chemical and physical properties, sources, and health effects of oxides of nitrogen (NO_x). Because much of this community is interested in accurately measuring NO_2 in order to monitor exposure levels and avoid adverse health effects, a significant effort was made to extract state-of-the-art methodologies and instrumentation from the current literature. Accurate analytical data is often dependent on the suitability of the analytical procedure to the sampling situation. It is hoped that the Appendix will provide the analyst with pertinent information on the various analytical techniques for measuring NO_2 so that the most appropriate one can be chosen for a particular sampling scenario.

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EXPLANATION OF THE APPENDICES

Appendix A is included to provide a quick guide of the different types of instrumentation discussed in the previous section. The range of concentrations listed for each type of monitor is meant to be representative of the method. Individual models may have capabilities outside the listed range. Therefore, there may be instruments commercially available that have capabilities superior or inferior to those listed on the chart.

A list of manufacturers who produce NO_x detectors is included in Appendix B. The list is not complete although an effort was made to include all known manufacturers. The authors apologize for omitting any manufacturers.

Appendix A: Methodology Characteristics of NO₂ Monitors

Method	Applications	Detection	Portability	Response Time	Recovery Time	Real Time	Cost (\$)	Notes
Colorimetric	a, e	500 ppb to 100 ppm	1 to 3	~few(s)	~few(s)	yes and no	200 - 1,000	low interference, linear, low maintenance, low training level required.
Chemiluminescence	a, e	0.002 ppm to 10,000ppm	2 to 4	< 2 s to 30 s	2 to 3 min.	no	5,000 to 10,000	very low interference, linear, low maintenance, low training level required.
Chromatography	a	0.1 ppb to 2000 ppm	1 to 5	3 s	< 1 min	no	3,000 to 12,000	very low interference, low to moderate maintenance, moderate to high training level required.
Electrochemical	a,d,e,f	0 to 100 ppm	1 to 5	< 10 s to < 30 s	< 30 s	yes	1,500 to 2,500	little interference, sensor life > 6 months (can be replaced separately) remote sensor capabilities, very low maintenance, low training level required.
Spectrophotometric	a,b,c,e,f	20 to 100% vol	2 to 5	< 2 s to < 15 s	none	yes	3,000 to 12,000	linear, very low interference, high training level required, moderate maintenance.
FIA Colorimetric Experimental Method	a,e	500 ppb to 100 ppm	2	< 6 s	~few(s)	yes	N/A	linear, low maintenance, low training level required.

Applications

a-accidental spills, ambient air, clean air control, environmental surveys\ monitoring, emergency response, waste site evaluation, source monitoring
b-automotive exhaust analysis
c-stack gas measurement
d-chemical process control
e-parking garage\ road tunnel monitoring control

Portability

1-hand held, with internal power supply
2-small desk top, with internal power supply
3-small desk top, with external power supply
4-floor model, with external power supply

APPENDIX B: ADDRESSES OF MANUFACTURERS

Advanced Chemical Sensors Company
350 Oaks Lane
Pompano Beach, FL 33069
(305) 979-0958

Air Dimensions, Inc.
1015 West Newport Center
Suite 101
Deerfield Beach, FL 33442
(800) 423-6464

American Gas and Chemical Company, Ltd.
220 Pegasus Avenue
Northvale, NJ 07647
(201) 767-7300

Anacon
19 Bartlett Street
Marlborough, MA 01752
(617) 481-7888

Anarad Analytical Instruments
534 East Ortega Street
Santa Barbara, CA 93103
(805) 963-6583

Anderson Samplers, Inc.
4215-T Wendell Drive
Atlanta, GA 30336
(213) 692-9021

Assay Technology
935 Industrial Avenue
Palo Alto, CA 94303
(415) 424-9947

Automated Custom Systems, Inc.
1238 West Grove Avenue
Orange, CA 92665
(714) 974-5560

Barringer Research, Ltd.
304 Carlingview Drive
Metropolitan Toronto
Rexdale, Ontario
Canada
(416) 675-3870

Beckman Industrial
996 Old Eagle School Road
Suite 1120
Wayne, PA 19087
(215) 688-7300

BGI, Inc.
58 Guinan Street
Waltham, MA 02154
(617) 891-9380

Captair
One Elm Square-Route 114
North Andover, MA 01845
(508) 975-3336

Catalyst Research
3706 Crondall Lane
Owings Mills, MD 21117
(301) 356-2400

CEA Instruments, Inc.
16 Chestnut Street
P.O. Box 303
Emerson, NJ 07630
(201) 967-5660

Chemical Data Systems
7000 Limestone Road
Oxford, PA 19363
(215) 932-3636

Columbia Scientific
Industries Corporation
11950 Jollyville Road
P.O. Box 203190
Austin, TX 78720
(512) 258-5191

Compur-Electronic
Steinerstra Be 15
8000 Munchen 70
West Germany

Comsip, Inc.
3030 Red Hat Lane
Whittier, CA 90601
(213) 692-9021

Control Instruments Corporation
25 Law Drive
Fairfield, NJ 07006
(201) 575-9114

Du Pont
Instruments Systems
Concord Plaza, Quillen Building
Wilmington, DE 19898
(302) 772-5481

Dynamation, Inc.
3784 Plaza Drive
Ann Arbor, MI 48108
(313) 769-1888

Dynatron, Inc.
P.O. Box 745
Wallingford, CT 06492
(800) 243-3124

Enmet Corporation
2308 S. Industrial Highway
P.O. Box 979
Ann Arbor, MI 48106
(313) 761-1270

Fischer and Porter Company
Warminster, PA 18974
(215) 674-6000

Fluid Management Systems, Inc.
40 Woodleigh Road
Watertown, MA 02172
(617) 926-1521

Foxboro Analytical
P.O. Box 5449
South Norwalk, CT 06856
(203) 853-1616

Gas Tech, Inc.
8445 Central Avenue
Newark, CA 94560
(415) 794-6200

Horiba Instruments, Inc.
Irvine Facility
1021 Duryea Avenue
Irvine, CA 92714
(714) 250-4811

Inficon Leybold-Heraeus, Inc.
6500 Fly Road
East Syracuse, NY 13057
(315) 453-0377

International Sensor Technology
17771 Fitch Street
Irvine, CA 92714
(714) 863-9999

Interscan Corporation
P.O. Box 2496-T
Chatsworth, CA 91313
(818) 882-2331

Isis Corporation
P.O. Box 9374
Wilmington, DE 19809
(302) 792-3300

Janos Technology, Inc.
Route 35
Townshend, VT 05353
(802) 365-7714

Lear Siegler, Inc.
Measurement Controls Division
74 Inverness Drive
East Englewood, CO 80112
(303) 792-3300

LFE
Instruments Division
55 Green Street
Clinton, MA 01510
(508) 835-1000

Matheson Gas Products
6655 Amberton Drive, Unit 0
Baltimore, MD 21227
(301) 796-0517

MDA Scientific, Inc.
405 Barclay Boulevard
Lincolnshire, IL 60069
(800) 323-2000

Metrosonics, Inc.
P.O. Box 23075
Rochester, NY 14692
(716) 334-7300

MJ Segal Associates
P.O. Box 661
Newtown, PA 18940
(215) 255-5566

Mobay Corporation
Mobay Road
Pittsburgh, PA 15205
(412) 777-2000

Monitor Labs
10180 Scropps Ranch Boulevard
San Diego, CA 92131
(619) 578-5060

Mott Metallurgical Corporation
Farmington Industrial Park
Farmington, CT 06032
(203) 677-7311

National Draeger, Inc.
101 Technology Drive
P.O. Box 120
Pittsburgh, PA 15230
(412) 787-8383

Neotronics N.A., Inc.
P.O. Box 370
2144 Hilton Drive, S.W.
Gainesville, GA 30503
(404) 535-0600

Nuclide Corporation
Nuclide Analysis Associates
642 East College Avenue
State College, PA 16801
(814) 238-0541

Photovac International, Inc.
741 Parks Avenue
Huntington Long Island, NY 11743
(516) 351-5809

Questron Corporation
P.O. Box 2387
Princeton, NJ 08540
(609) 587-6898

Rexnord Automation
Gas Detection Division
207 Java Drive
Sunnyvale, CA 94089
(408) 734-1221

Scintrex
222 Snidercroft Road
Concord, Ontario
Canada LAK 1B5
(416) 669-2280

Sensidyne, Inc.
12345 Starkey Road, Suite E
Largo, FL 34643
(800) 451-9444

Sierra Instruments
Sierra Building
25 Pilot Road
P.O. Box 909
Carmel Valley, CA 93924
(800) 345-TRAK

Sierra Monitor Corporation
1991 Tarob Court
Milpitas, CA 95035
(408) 262-6611

SKC, Inc.
334 Valley View Road
Eighty Four, PA 15330
(412) 941-9701

Spectra-Physics
Laser Analytics Division
25 Wiggins Avenue
Bedford, MA 01730
(617) 275-2650

Sunshine Scientific Instruments, Inc.
1810 Grant Avenue
Philadelphia, PA 19115
(215) 673-6500

Thermo Environmental Instruments, Inc.
8 West Forge Parkway
Franklin, MA 02038
(617) 520-0430

Tracor Atlas, Inc.
9441 Baythorne Drive
Houston, TX 77041
(713) 462-6116

Tylan
23301 S. Wilmington Avenue
Carson, CA 90745
(213) 518-3610

Wescan Instruments, Inc.
2051 Waukegan Road
Deerfield, IL 60015
(800) 642-4667

Westinghouse Electric Corporation
Process and Environmental
Measuring Technology
Orrville, OH 44667
(216) 682-9010

Wisa Precision Pumps USA, Inc.
235 West First Street
Bayonne, NJ 07002

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